

***THE EFFECT OF SURFACE TENSION (KELVIN EFFECT) ON  
THE EQUILIBRIUM RADIUS OF A HYGROSCOPIC  
AQUEOUS AEROSOL PARTICLE***

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## Nomenclature

$a_w$	water activity
$\Delta a_w$	change in water activity at given $h$ due to Kelvin effect
$c$	constant in power law
$C$	constant in expression of Fitzgerald (1975)
$f$	resonant frequency of shape oscillation of drop
$g$	hygroscopic growth factor
$h$	fractional relative humidity ( $\equiv RH/100\%$ )
$h_e$	value of $h$ at which efflorescence (crystallization) occurs
$h_{5\%}$	value of $h$ at which Kelvin effect results in 5% decrease in radius
$j$	mode number of drop oscillation
$M_w$	molar mass of water ( $0.018 \text{ kg mol}^{-1}$ )
$m_{\text{dry}}$	dry mass of (anhydrous) solute
$n$	exponent in power law
$q$	charge on a suspended drop
RH	percent relative humidity
$R$	gas constant ( $8.3 \text{ J K}^{-1} \text{ mol}^{-1}$ )
$r$	drop radius
$\Delta r$	change in radius due to Kelvin effect
$r_{\text{dry}}$	volume-equivalent dry radius
$r_{\text{dry},5\%}$	value of $r_{\text{dry}}$ at which Kelvin effect results in 5% decrease in radius
$r_\sigma$	characteristic length scale for Kelvin effect
$r_{\sigma,0}$	value of $r_\sigma$ evaluated for pure water ( $\approx 1.1 \text{ nm}$ )
$T$	temperature
$\bar{v}_w$	partial molal volume of water in solution
$\bar{v}_{w,0}$	partial molal volume of pure water ( $\approx 1.8 \cdot 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ )
$\alpha$	function of relative humidity in expression of Fitzgerald (1975)
$\beta$	function of relative humidity in expression of Fitzgerald (1975)
$\varepsilon$	dielectric constant of solution
$\varepsilon_0$	electric constant ( $\approx 8.85 \cdot 10^{-12} \text{ F m}^{-1}$ )
$\Phi$	function of relative humidity in expression of Fitzgerald (1975)
$\rho_{\text{dry}}$	density of (anhydrous) solute
$\rho_w$	density of pure water ( $\approx 1.0 \cdot 10^3 \text{ kg m}^{-3}$ )
$\sigma$	surface tension of solution-air interface
$\Delta \sigma$	difference in surface tension from that of pure water due to solute
$\sigma_w$	surface tension of pure water-air interface ( $\approx 7.4 \cdot 10^{-2} \text{ J m}^{-2}$ )
$\tau$	characteristic time for rate of exponential decay of drop oscillation
$\nu$	kinematic viscosity of solution
$\xi$	radius ratio relative to volume-equivalent dry radius ( $\equiv r/r_{\text{dry}}$ )
$\Delta \xi$	change in radius ratio due to Kelvin effect
$\xi_\sigma$	ratio of characteristic length scale for Kelvin effect to $r_{\text{dry}}$ ( $\equiv r_\sigma/r_{\text{dry}}$ )

## Abstract

The effect of surface tension (the Kelvin effect) on the equilibrium radius of an aqueous solution drop for fractional relative humidity  $h$  less than unity is analyzed mathematically. Expressions for the lowest-order corrections to the equilibrium radius and to the radius ratio (relative to the volume-equivalent dry radius) due to the Kelvin effect are presented and compared with data for solution drops of ammonium sulfate and sodium chloride. To lowest order the decrease in radius resulting from the Kelvin effect is independent of  $r_{\text{dry}}$  and depends only on  $h$ . This decrease is approximated to good accuracy by  $-\Delta r/\text{nm} = (h/3)/(1-h)$ , with only a weak dependence on solute and on temperature. The importance of the Kelvin effect on drop radius is further quantified in several ways. The value of the volume-equivalent dry radius below which the Kelvin effect results in more than a 5% decrease in the equilibrium radius of a solution drop at a given relative humidity  $h$  is given approximately by  $r_{\text{dry},5\%}/\text{nm} = [8h/(1-h)^{2/3}]$ . The decrease in the hygroscopic growth factor  $g$  of an aqueous solution drop between a low relative humidity and  $h = 0.9$  caused by the Kelvin effect is given approximately by  $\Delta g = -3 \text{ nm}/r_{\text{dry}}$ , again with only a weak dependence on solute and on temperature. These approximations compare well with observed measurements of growth factors for dry radius as low as 10 nm. Central to this analysis and to each of these results is the introduction of the characteristic length scale for the effects of surface tension,  $r_\sigma \equiv 2 \bar{v}_w \sigma/(RT)$ , where  $\bar{v}_w$  is the partial molal volume of water in the solution,  $\sigma$  the surface tension of the solution-air interface,  $R$  the gas constant, and  $T$  the absolute temperature. For dilute aqueous solutions at room temperature  $r_\sigma$  is approximately 1.1 nm. These findings, all of which are presented for fractional relative humidity as the independent variable, allow the magnitude of the Kelvin effect and its consequences on the properties of an aqueous solution drop to be readily assessed.

## Keywords:

Kelvin effect, surface tension, hygroscopicity, relative humidity, growth factor

## 1. Introduction

The vapor pressure of water in equilibrium with an aqueous solution drop depends on the solute and its concentration and on the size of the drop (Köhler, 1936; Wright, 1936). This size dependence, which is due to the surface tension of the solution-air interface, is known as the Kelvin effect (Thomson, 1871). For an aqueous solution drop with given solute and concentration the equilibrium vapor pressure of water (equal to the fractional relative humidity  $h \equiv RH/100\%$ ) increases with decreasing drop radius; conversely, at a given relative humidity the equilibrium radius of such a drop is less than what it would be if surface tension had no effect. The Kelvin effect is of central importance to cloud drop activation, and as the equilibrium radius is a key property of an atmospheric aerosol particle, affecting its light-scattering behavior, dry deposition, and the like, the Kelvin effect can also play an important role in other atmospheric processes. This paper examines the Kelvin effect and the quantities upon which it depends. An expression is derived for the decrease in the equilibrium radius of a solution drop due to the Kelvin effect, and estimates are presented for the Kelvin effect in various situations.

The vapor pressure of water in equilibrium with an aqueous solution drop with radius  $r$  is greater than the water activity  $a_w$  in the drop by the factor  $\exp\{2\bar{v}_w\sigma/(RT\bar{r})\}$ , where  $\bar{v}_w$  is the partial molal volume of water in the solution (Lewis and Randall, 1961),  $\sigma$  the surface tension of the solution-air interface,  $R$  the gas constant, and  $T$  the absolute temperature (Tang, 1976). The quantities  $\bar{v}_w$  and  $\sigma$  depend on the solute and its concentration, and weakly on the temperature. The solute concentration can be described in a variety of ways, such as the molality or solute mass fraction. One particularly useful way of unambiguously specifying this concentration is the radius ratio  $\xi \equiv r/r_{\text{dry}}$ , the ratio of the radius of the drop  $r$  to the volume-equivalent dry radius  $r_{\text{dry}}$ , which is defined in terms of the mass of solute in the drop  $m_{\text{dry}}$  and the bulk dry density of the (anhydrous) solute  $\rho_{\text{dry}}$  by  $r_{\text{dry}} = [3m_{\text{dry}}/(4\pi\rho_{\text{dry}})]^{1/3}$ . While a concern with this definition might be that  $\rho_{\text{dry}}$ , and thus the relationship between  $m_{\text{dry}}$  and  $r_{\text{dry}}$ , may depend on the crystalline state of the dry material, in practice  $r_{\text{dry}}$  is not very sensitive to the value used for  $\rho_{\text{dry}}$ , both because of the cube root dependence of  $r_{\text{dry}}$  upon  $\rho_{\text{dry}}$  (resulting in any fractional uncertainty in  $r_{\text{dry}}$  being one-third less than that in  $\rho_{\text{dry}}$ ), and because in many situations it is not the radius ratio itself that is of interest, but rather the so-called hygroscopic growth factor  $g$ , which is the ratio of the radii (or radius ratios) at two values of  $h$  and hence independent of  $\rho_{\text{dry}}$ . The quantity  $r_{\text{dry}}$  is not necessarily equal to the physical radius of a dried particle, as such a particle may not be spherical, may contain some residual water, and may have a density different from that of the bulk solute because of voids, for instance. Nevertheless,  $r_{\text{dry}}$  is an unambiguous measure of the mass of solute contained in the particle and provides a physically meaningful representation of its size.

The Kelvin effect on the equilibrium relative humidity of an aqueous solution drop containing an amount of solute specified by  $r_{\text{dry}}$  is described by

$$h = a_w(\xi) \exp \left\{ \frac{2\bar{v}_w(\xi)\sigma(\xi)}{RT\xi r_{\text{dry}}} \right\}, \quad (1)$$

where the dependencies of the several quantities upon the solute concentration are explicitly shown as dependencies on  $\xi$ . With the definitions  $r_\sigma \equiv 2 \bar{v}_w \sigma / (RT)$  and  $\xi_\sigma \equiv r_\sigma / r_{\text{dry}}$  this equation becomes

$$h = a_w(\xi) \exp\left(\frac{r_\sigma}{r}\right), \quad (2)$$

or equivalently

$$h = a_w(\xi) \exp\left(\frac{\xi_\sigma}{\xi}\right), \quad (3)$$

which can be inverted to yield an expression for the water activity in terms of the fractional relative humidity  $h$ ,

$$a_w(\xi) = h \exp\left(\frac{-\xi_\sigma}{\xi}\right). \quad (4)$$

The quantity  $r_\sigma$  depends on the solute and its concentration through dependencies of the partial molal volume of water in solution  $\bar{v}_w$  and the surface tension of the solution-air interface  $\sigma$  on solute and concentration. Typically, with increasing solute concentration (decreasing  $h$ )  $\bar{v}_w$  decreases, but  $\sigma$  increases more rapidly, resulting in  $r_\sigma$  being an increasing function of solute concentration (and a decreasing function of  $h$ ). The quantity  $r_{\sigma,0}$  is defined as the value of  $r_\sigma$  calculated with  $\bar{v}_w$  and  $\sigma$  taken as their values at infinite dilution,  $\bar{v}_{w,0}$  ( $\equiv M_w / \rho_w$ , the ratio of the molar mass of water to the density of pure water) and  $\sigma_w$  (the surface tension of the pure water-air interface), respectively; the two quantities being related by  $r_\sigma = r_{\sigma,0} (\bar{v}_w / \bar{v}_{w,0}) (\sigma / \sigma_w)$ . The quantities  $r_\sigma$  and  $r_{\sigma,0}$  depend weakly on temperature, both directly (through the factor  $T$  in the denominator) and indirectly through the dependencies of  $\bar{v}_w$  and  $\sigma$  on temperature. The quantity  $r_{\sigma,0}$  takes values 1.20 nm at 0°C and 1.05 nm at 25°C; in numerical results below the value 1.1 nm is used.

The Kelvin effect is manifested by the dependence of the relationship between  $\xi$  and  $h$  on  $r_{\text{dry}}$ . As both  $\xi$  and  $h$  are dimensionless, quantitative description of the Kelvin effect requires an additional quantity of dimension length to form a dimensionless group containing  $r_{\text{dry}}$ . Such a quantity is  $r_\sigma$ , which provides a characteristic length scale for the effect of surface tension (i.e., the Kelvin effect) and permits formation of the dimensionless group  $r_\sigma / r_{\text{dry}}$ . From Eq. 1 it is seen that vanishingly small surface tension (or  $r_\sigma$ ) is mathematically equivalent to infinitely large  $r_{\text{dry}}$ , i.e., bulk solution. Physically it is necessary that for a given  $h$  the radius ratio approach a limiting value with increasing  $r_{\text{dry}}$ , equal to that in the absence of the Kelvin effect, as with increasing  $r_{\text{dry}}$  the effect of surface tension becomes increasingly less important. Hence for increasing  $r_{\text{dry}}$  the magnitude of the decrease in the radius ratio due to the Kelvin effect must decrease toward zero.

The amount by which the fractional relative humidity in equilibrium with a drop of given solute concentration is larger than the water activity because of the Kelvin effect is given by

$$\Delta h = h - a_w(\xi) = h \left[ 1 - e^{-\xi_\sigma / \xi} \right]. \quad (5)$$

Expansion of the exponential yields

$$1 - e^{-\xi_\sigma/\xi} = \frac{\xi_\sigma}{\xi} + \dots;$$

when only the first term is kept this expression is accurate to within ~10% for  $r > 5$  nm. Substitution of this expression into Eq. 5 and retention of only the lowest-order term in  $\xi_\sigma$  yields the lowest-order correction to the relative humidity due to the Kelvin effect

$$\Delta h = h \frac{\xi_\sigma}{\xi}, \quad (6)$$

or equivalently

$$\Delta h = h \frac{r_\sigma}{r}.$$

As expected, this increase in the fractional relative humidity is positive and decreases with increasing particle size.

Although the value of  $h$  for a given radius ratio  $\xi$  may be obtained from Eq. 1, in many situations it is desirable to determine  $\xi$  for a given  $h$ , as the relative humidity is often externally imposed and hence is the controlling variable. For situations in which the Kelvin effect can be neglected, such as bulk solutions and sufficiently large drops, the exponential factor in Eq. 1 can be taken as unity, the water activity is equal to the fractional relative humidity ( $a_w = h$ ), and a relation of the form  $a_w = a_w(\xi)$  can (at least in principle) be inverted to yield  $\xi = \xi(a_w) = \xi(h)$ . For situations in which the Kelvin effect cannot be neglected it is necessary to invert Eq. 1 to yield an expression for  $\xi$  as a function of  $h$  and  $r_{\text{dry}}$ ,  $\xi = \xi(h, r_{\text{dry}})$ , the Kelvin effect being manifested in the dependence of  $\xi$  on  $r_{\text{dry}}$ . Determination of such an expression is a bit more involved, but an approximation can be obtained which not only yields the lowest-order correction to  $\xi(h)$ , *i.e.*, the term containing the factor  $\xi_\sigma$  in the difference  $\xi(h, r_{\text{dry}}) - \xi(h, \infty)$ , but additionally allows determination of the range of conditions for which this approximation exhibits a specific accuracy. For values of  $h$  equal to or greater than unity the Kelvin effect is not a small perturbation but in fact is the reason that the radius of the drop does not become infinitely large; hence the discussion here is necessarily limited to  $h < 1$ .

## 2. Lowest-Order Corrections to Radius and Radius Ratio Due to Kelvin Effect

### 2.1 Derivation

The equilibrium radius ratio of a solution drop at a given relative humidity calculated without taking into account the Kelvin effect can be calculated from the solute concentration, or equivalently the water activity, and as noted above can be represented (at least in principle) by an expression of the form  $\xi(a_w)$ , or equivalently  $\xi(h)$ . The change  $\Delta\xi$  in the radius ratio of a solution drop due to the Kelvin effect at fractional relative humidity  $h$  is the difference between the radius ratio calculated for water activity  $a_w$  ( $=h \exp(-\xi_\sigma/\xi)$ ) and that calculated for  $h$ :

$$\Delta\xi \equiv \xi\left(h e^{-\xi_\sigma/\xi}\right) - \xi(h) = \left(\frac{d\xi}{dh}\right) \left[ h \left( e^{-\xi_\sigma/\xi} - 1 \right) \right] + \dots \quad (7)$$

Upon expansion of the exponential, as above, and substitution into Eq. 7, with retention of only the lowest-order term in  $\xi_\sigma$ , the lowest-order correction to the radius ratio due to the Kelvin effect can be determined as

$$\Delta\xi = -\xi_\sigma \frac{h}{\xi} \frac{d\xi}{dh}, \quad (8)$$

where  $\xi$  and  $d\xi/dh$  are evaluated for the bulk solution (*i.e.*, without taking into account the Kelvin effect). Upon change of variable from  $h$  to  $1-h$  this expression can be transformed into a form that proves useful because it explicitly represents the dependence of  $\Delta\xi$  on  $h$  as  $h$  approaches unity,

$$\Delta\xi = \xi_\sigma \left( \frac{h}{1-h} \right) \left[ \frac{d \ln \xi}{d \ln(1-h)} \right]. \quad (9)$$

The lowest-order correction to the radius of a solution drop due to the Kelvin effect is given by

$$\Delta r = -r_\sigma \frac{h}{\xi} \frac{d\xi}{dh}, \quad (10)$$

which can alternatively be expressed as

$$\Delta r = r_\sigma \left( \frac{h}{1-h} \right) \left[ \frac{d \ln \xi}{d \ln(1-h)} \right]. \quad (11)$$

As  $\xi$  is an increasing function of  $h$  (and hence a decreasing function of  $1-h$ ), the lowest-order corrections to the radius ratio and radius due to the Kelvin effect are negative, consistent with the decrease in the radius (and radius ratio) due to the Kelvin effect. More importantly, for a given solute the quantities  $\xi$  and  $d\xi/dh$ , or  $d\xi/d(1-h)$ , depend only on the concentration and hence (to lowest order) may be expressed as functions only of  $h$ ; likewise  $r_\sigma$  depends only on  $h$  (through the dependencies on solute concentration of  $\bar{v}_w$  and  $\sigma$ ). Thus to lowest order the decrease in the radius resulting from the Kelvin effect depends only on  $h$  and is independent of  $r_{\text{dry}}$ , or equivalently, of the amount of solute in the drop.

## 2.2 Kelvin Correction for a Power Law Dependence of Radius Ratio on $1-h$

Calculation of the lowest-order Kelvin correction to the radius or radius ratio requires knowledge of the dependence of  $\xi$  on  $h$ . Numerous expressions have been presented for this dependence; for solutions of many inorganic substances  $\xi$  can be accurately approximated over wide ranges of relative humidity by a two-parameter power law in  $1-h$

$$\xi \equiv \frac{r}{r_{\text{dry}}} = \frac{c}{(1-h)^n}, \quad (12)$$

a form first used by Keith and Arons (1954) for sea salt aerosol particles and later by Kasten (1969) for other aerosol particles. The values of  $c$  and  $n$  depend on the solute and on the range of relative humidity;  $c$  is typically near unity and  $n$  is typically in the range 0.20-0.33, taking values near 1/3 at high relative humidity, consistent with vapor-pressure lowering given by Raoult's Law (Lewis and Randall, 1961). Radius ratios are presented

in Fig. 1 for solution drops of ammonium sulfate,  $(\text{NH}_4)_2\text{SO}_4$ , and sodium chloride,  $\text{NaCl}$ , two common constituents of atmospheric aerosol particles, in two ranges of fractional relative humidity,  $h_e < h < 0.90$  (where  $h_e$  is the efflorescence, or crystallization, relative humidity, below which solution drops do not exist), and  $0.90 < h < 0.995$  (the upper limit of measurements); the corresponding values of  $c$  and  $n$  are presented in Table 1. Also shown are the errors of these expressions. Pertinent properties of solution drops of these substances have been studied by numerous investigators and are quite well characterized. The humidity dependence of the radius ratios of drops of many other inorganic salts of atmospheric importance (including sulfuric acid) are very similar or intermediate to those of these two substances over a wide range of relative humidity (see for instance Fig. 4 of Tang, 1996); thus the behavior of these two substances provides an indication of the range of behavior that can be expected for other inorganic salts. For the lower relative humidity range the uncertainty in the measurements themselves is  $\sim 1\%$ . For the higher relative humidity range much of the uncertainty in this parameterization results from the strong departure from ideality due to the electrolytic nature of the ionic solutions; greater accuracy would require a much more complicated expression (Lewis, 2006). The sensitivity of  $\xi$  to measurement uncertainty may be assessed by noting that for  $h > 0.90$  an uncertainty in  $h$  of only 0.01 would result in uncertainty in  $\xi$  of at least 3%; equivalently, as the equilibrium vapor pressure of water increases by approximately 6% per  $^\circ\text{C}$ , an uncertainty in  $\xi$  of less than 3% would require an uncertainty in temperature of less than  $\sim 0.15^\circ\text{C}$ . Hence the accuracies of the approximate expressions would appear to be sufficient for most atmospheric applications.

Evaluation of the lowest-order corrections to the radius ratio (Eq. 9) and to the radius (Eq. 11) is facilitated by the power-law relation between  $\xi$  and  $1-h$  given by Eq. 12, as for such a relation  $d\ln\xi/d\ln(1-h) = -n$ , from which the lowest-order correction to the radius ratio is readily obtained as

$$\Delta\xi = -\xi_\sigma \frac{nh}{1-h} \quad (13)$$

and the lowest-order correction to the radius as

$$\Delta r = -r_\sigma \frac{nh}{1-h}. \quad (14)$$

Estimates for  $\Delta r$  can be obtained through substitution of  $r_{\sigma,0}$  ( $\approx 1.1$  nm) for  $r_\sigma$  and the choice  $n = 0.3$  as a typical value to yield

$$\frac{\Delta r}{\text{nm}} \approx \frac{-h/3}{1-h}; \quad (15)$$

this radius correction is shown in Fig. 2. For  $h=(0.75, 0.9, 0.95, 0.99)$  this expression yields  $\Delta r = -(1, 3, 6, 33)$  nm, again independent of  $r_{\text{dry}}$ . Although the exact values depend somewhat on the choice for  $n$ , this expression gives an indication of the magnitude of the Kelvin correction to the equilibrium radius. As noted above, the quantity  $r_\sigma$  depends only on  $h$  (through the dependencies of  $\bar{v}_w$  and  $\sigma$  on solute concentration), and with

decreasing  $h$  (increasing solute concentration) the quantity  $r_\sigma$  increases. However, the decrease in the exponent  $n$  with decreasing  $h$  (Table 1) somewhat compensates for the increase in  $r_\sigma$  so that their product exhibits much less of a dependence on  $h$  than either quantity separately. As expected, the magnitude of the lowest-order correction in radius ratio (or radius) due to the Kelvin effect for a given dry radius increases with increasing



relative humidity, especially as  $h$  approaches unity. Additionally, as the magnitude of this correction increases with increasing  $h$  faster than the radius ratio (or radius) itself, the fractional change in radius ratio (or radius), and thus the importance of the Kelvin correction, increase with increasing relative humidity.

Also shown in Fig. 2 are values of the lowest-order decrease in radius  $-\Delta r$  due to the Kelvin effect for solution drops of ammonium sulfate and sodium chloride determined from Eq. 1, evaluated with the dependencies on solute concentration of both the partial molal volume of water in the solution  $\bar{v}_w$  and the surface tension of the solution-air interface  $\sigma$ , and hence of  $r_\sigma$ , explicitly taken into account (as discussed in Appendix 1). These results indicate that the lowest-order correction to the radius resulting from the Kelvin effect is only weakly dependent on solute. Furthermore these results demonstrate that over the entire range of  $h$  up to very near unity the simple expression given by Eq. 15 provides a highly accurate approximation to the decrease in drop radius due to the Kelvin effect.

The decreases in the radii of ammonium sulfate and sodium chloride solution drops with  $r_{\text{dry}} = 10$  nm and 25 nm calculated from Eq. 1, taking into account the dependencies of  $\bar{v}_w$  and  $\sigma$  on concentration, are also shown in Fig. 2. These decreases are very nearly the same for these two substances, and for a wide range of  $h$  they are very nearly equal to those given by the lowest-order correction. For values of  $h$  approaching unity the decreases calculated from Eq. 1 are less than those given by Eq. 10, implying that the lowest-order correction is an upper bound to the magnitude of the decrease. This discrepancy is not surprising, as can be seen by the following example. At  $h = 0.995$  the lowest-order decrease for sodium chloride solution drops evaluated from Eq. 10 is approximately 70 nm, whereas the decrease calculated from Eq. 1 is only ~50 nm for drops with  $r_{\text{dry}} = 25$  nm, and only ~30 nm for drops with  $r_{\text{dry}} = 10$  nm. However, at this value of  $h$  the radius of the drop with  $r_{\text{dry}} = 25$  nm is only ~105 nm, and that for  $r_{\text{dry}} = 10$  nm is only ~32 nm, so in these situations the lowest-order correction to the radius is a substantial fraction of the drop radius itself. It would thus not be expected that under such circumstances the lowest-order correction would provide accurate results. Although situations such as these require inclusion of additional (*i.e.*, higher-order) terms for accurate results, this approach is neither feasible nor useful, and an alternative approach is required (Lewis, 2006).

### 2.3 Range of Validity of Using Only the Lowest-order Correction to the Radius Ratio

As the fractional relative humidity  $h$  increases, the decrease in equilibrium radius of a solution drop with given  $r_{\text{dry}}$  due to the Kelvin effect becomes increasingly greater. For large  $h$  the approximation that the radius ratio is equal to that of the bulk solution minus the lowest-order correction becomes increasingly inaccurate as higher-order terms become important. This is illustrated in Fig. 3, which shows radius ratio for a bulk solution of ammonium sulfate, that for ammonium sulfate solution drops with  $r_{\text{dry}}$  values of 5, 10, and 25 nm calculated from Eq. 1, and that calculated using Eq. 8 as the lowest-order corrections from the bulk solution. (For the radius ratios of the solution drops the dependencies on solute concentration of both the partial molal volume of water in the solution  $\bar{v}_w$  and the surface tension of the solution-air interface  $\sigma$ , and hence of  $r_\sigma$ , are

explicitly taken into account as discussed above; solutions with radius ratios  $\xi$  less than 1.49 are supersaturated with respect to the solute.) For a given fractional relative humidity  $h$  the magnitude of the decrease in radius ratio due to the Kelvin effect increases with decreasing  $r_{\text{dry}}$ , and for a given  $r_{\text{dry}}$  the magnitude of the decrease increases with increasing  $h$ . At low  $h$  the radius ratio for drops of each of these sizes is near the bulk value, and the decrease in radius ratio due to the Kelvin effect is accurately approximated by the lowest-order correction, but with increasing  $h$ , the radius ratio become increasingly less than the bulk value, and the decrease in the radius ratio due to the Kelvin effect is increasingly overestimated by the lowest-order correction. For sufficiently high values of  $h$ , which increase with increasing  $r_{\text{dry}}$  from near 0.82 for  $r_{\text{dry}} = 5$  nm to near 0.92 for 10 nm to near 0.99 for 25 nm, the radius ratio calculated using only the lowest-order correction from the bulk value reaches a maximum value and decreases with further increase in  $h$ . For larger values of  $h$  the magnitude of the lowest-order correction to the radius ratio due to the Kelvin effect, which varies approximately as  $(1-h)^{-1}$ , increases much faster than the radius ratio itself, which varies approximately as  $(1-h)^{-1/3}$ , and the lowest-order correction rapidly becomes an appreciable fraction of the radius ratio itself. In these situations higher-order terms, which also become very large, contribute appreciably to the radius ratio.

The range of validity of using only the lowest-order Kelvin correction to the radius ratio from the bulk solution value can be ascertained by examination of the relationship between the fractional relative humidity  $h$  and the volume-equivalent dry radius  $r_{\text{dry}}$  for which this correction is a given fraction of the radius itself. Although the relationship will of course depend on the value chosen for the fraction, the (arbitrary) choice of 5% is made here, with the corresponding value of the dry radius denoted  $r_{\text{dry},5\%}$ . For a power-law dependence of  $\xi$  on  $1-h$  given by Eq. 12, the fractional change in the radius, or radius ratio, due to the Kelvin effect can be obtained from Eq. 13 (or 14) as

$$\frac{\Delta r}{r} \equiv \frac{\Delta \xi}{\xi} = \frac{-\xi_{\sigma} \frac{nh}{1-h}}{\frac{c}{(1-h)^n}} = -\frac{r_{\sigma}}{r_{\text{dry}}} \frac{n}{c} \frac{h}{(1-h)^{1-n}}, \quad (16)$$

where  $r_{\sigma}$  depends on the concentration (radius ratio) and thus on  $h$ . Eq. 16 can be inverted to determine the value of  $r_{\text{dry}}$  for which the Kelvin effect makes a 5% decrease in the radius ratio:

$$r_{\text{dry},5\%} = \frac{r_{\sigma}}{0.05} \frac{n}{c} \frac{h}{(1-h)^{1-n}}. \quad (17)$$

For  $r_{\text{dry}} < r_{\text{dry},5\%}$  the Kelvin effect results in a decrease in the radius that is more than 5%. With the value of  $r_{\sigma}$  taken as  $r_{\sigma,0}$  (the value for pure water,  $\approx 1.1$  nm) and for  $n = 1/3$  and  $c = 0.95$ , intermediate to the values for ammonium sulfate solutions and sodium chloride solutions (Table 1), Eq. 17 yields the estimate

$$\frac{r_{\text{dry},5\%}}{\text{nm}} \approx \frac{8h}{(1-h)^{2/3}}, \quad (18)$$

shown in Fig. 4. As for  $\Delta r$  (Eq. 15 and Fig. 2), the increase in  $r_\sigma$  and the decrease in  $n$  with decreasing  $h$  (increasing solute concentration) are such that their product exhibits less of a dependence on  $h$  than either quantity alone.

Values of  $r_{\text{dry},5\%}$  are also shown in Fig. 4 for solution drops of ammonium sulfate and sodium chloride determined from Eq. 1, evaluated as in Fig. 1 with the dependencies on solute concentration of both the partial molal volume of water in the solution  $\bar{v}_w$  and the surface tension of the solution-air interface  $\sigma$ , and hence  $r_\sigma$ , explicitly taken into account as described above. As  $r_{\text{dry},5\%}$  is less than  $\sim 15$  nm for values of  $h$  below 0.75-0.80 (in which range extrapolations are required for surface tension and thus for  $r_\sigma$ ), the consequences of uncertainty in these extrapolations is unimportant for a wide range of drops sizes. At fractional relative humidity  $h = (0.75, 0.90, 0.95, 0.99)$  Eq. 18 yields values of  $r_{\text{dry},5\%}$  of approximately (15, 35, 55, 170) nm. Although the exact values depend on the choices for  $n$  and  $c$ , and although the approximation of  $r_{\sigma,0}$  for  $r_\sigma$  becomes increasingly inaccurate as  $h$  decreases, these values of  $r_{\text{dry},5\%}$  give an indication of the range for which the Kelvin effect becomes significant. For very small solution drops—those with  $r_{\text{dry}} < 10$ -20 nm, equivalent to  $r < 15$ -35 nm—this result implies that the lowest-order correction to the radius remains less than  $\sim 5\%$  only at low relative humidities, and therefore that under most situations in the atmosphere the Kelvin effect plays a large role in determining the size of such drops. Hence for such small drops application of formulations relating radius (or radius ratio) and relative humidity based on bulk solutions will result in substantial error.

It is also desired have an expression for the value of relative humidity  $h_{5\%}$  at a given  $r_{\text{dry}}$  above which neglect of the Kelvin effect results in more than a 5% decrease in the radius or radius ratio. In principle such an expression might be obtained by inverting Eq. 16 (or 18), but this is not in general possible. However, an estimate for this value (which provides a lower bound) can be obtained by taking  $h$  to be unity in the numerator of Eq. 16, yielding

$$h_{5\%} > 1 - \left[ \frac{1}{0.05} \frac{n}{c} \frac{r_\sigma}{r_{\text{dry}}} \right]^{1/(1-n)}. \quad (19)$$

For  $h > h_{5\%}$  the decrease in the radius due to the Kelvin effect is greater than 5%. For the choices  $n = 1/3$  and  $c = 0.95$ , as above, again with  $r_\sigma$  taken as  $r_{\sigma,0}$ , Eq. 19 yields  $h_{5\%} > (0.83, 0.94, 0.98)$  for  $r_{\text{dry}} = (25, 50, 100)$  nm, compared to the values  $h_{5\%} = (0.85, 0.94, 0.98)$  nm determined from Eq. 16.

#### 2.4 Application to Hygroscopic Growth Factor

The results for the lowest-order correction to the radius ratio can also be used to estimate the importance of the Kelvin effect on the hygroscopic growth factor  $g \equiv g(h_1, h_2)$ , defined as the ratio of the radius at relative humidity  $h_2$  to that at  $h_1$ . This growth factor is related to the radius ratio relative to  $r_{\text{dry}}$ ,  $\xi(h)$ , by

$$g(h_1, h_2) \equiv \frac{r(h_2)}{r(h_1)} = \frac{\xi(h_2)}{\xi(h_1)}. \quad (20)$$

The measured growth factor for  $h_1=0$ ,  $g(0, h_2)$ , is not necessarily equal to the radius ratio at  $h_2$ ,  $\xi(h_2)$ , because the measured radius at sufficiently low relative humidity that the

particle is ostensibly dry is not necessarily equal to the volume-equivalent dry radius  $r_{\text{dry}}$  for reasons noted above; however, these two quantities are expected to be comparable.

Measurements of the hygroscopic growth factors of atmospheric aerosol particles made with a tandem differential mobility analyzer (TDMA) have been used to infer particle composition (*e.g.*, McMurry and Stolzenburg, 1989; Zhang *et al.*, 1993; Covert and Heintzenberg, 1993; Svenningsson *et al.*, 1997; Berg *et al.*, 1998; Swietlicki *et al.*, 2000; Gasparini *et al.*, 2004). Particles consisting mostly of sodium chloride (such as sea salt aerosol particles) exhibit larger growth factors (by ~40%) than particles consisting mostly of sulfate, and particles consisting mainly of nonhygroscopic carbonaceous substances or crustal materials exhibit growth factors near unity. For example, the values of  $\xi(0.9)$  for bulk solutions of sodium chloride and ammonium sulfate, approximately equal to the growth factors from a much lower relative humidity to  $h = 0.9$ , are 2.4 and 1.7, respectively. Commonly  $g$  is examined as a function of the radius of the dried particle to assess possible dependence of composition on this radius, with radii as low as 25 nm reported by McMurry and Stolzenburg, by Zhang *et al.*, and by Svenningsson *et al.*, 17.5 nm by Berg *et al.* and by Swietlicki *et al.*, and 12 nm by Gasparini *et al.* Thus it is necessary to examine the influence of the Kelvin effect on the growth factor  $g$  as a function of  $r_{\text{dry}}$ .

The lowest-order correction to the growth factor  $g(h_1, h_2)$  resulting from the Kelvin effect can be determined from Eq. 20 as

$$\Delta g(h_1, h_2) = g(h_1, h_2) \left[ \frac{\Delta \xi(h_2)}{\xi(h_2)} - \frac{\Delta \xi(h_1)}{\xi(h_1)} \right]. \quad (21)$$

Evaluation of this correction in field situations is complicated by the fact that atmospheric aerosol particles for which hygroscopic growth factors are typically measured have unknown compositions, which may differ from particle to particle, and thus unknown functional relations  $\xi = \xi(h)$ , which likewise may differ from particle to particle. However, an accurate estimate for the Kelvin effect on the hygroscopic growth factor can be confidently obtained from the results above given the weak dependence of  $\Delta r$  on solute.

The value of  $h_2$  is typically chosen near 0.9 and that of  $h_1$  to be below the efflorescence relative humidity so that the particle is dry, in which situation there is no contribution from  $\Delta \xi(h_1)$ ; in any event the contribution from this term is typically much less than that from  $\Delta \xi(h_2)$ , and thus the choice of  $h_1$  is of little consequence. Hence the value of  $\Delta g(h_1, h_2)$  given by Eq. 21 is approximately equal to  $g(h_1, h_2)[\Delta \xi(h_2)/\xi(h_2)]$ , or equivalently,  $\Delta \xi(h_2)/\xi(h_1)$ . Although as noted above  $\xi(h_1)$  is not necessarily equal to unity, even for a completely dry particle, it is generally not very different from unity, and to fair approximation  $\Delta g(h_1, h_2) \approx \Delta \xi(h_2)$ . The decrease in the growth factor resulting from the Kelvin effect can therefore be evaluated using Eq. 13 as

$$\Delta g(0.4, 0.9) \approx \frac{-3 \text{ nm}}{r_{\text{dry}}}, \quad (22)$$

again with only a weak dependence on solute.

As the growth factor depends on the dry radius of the drop, failure to take into account the Kelvin effect on drop radius might result in attribution of differences in growth factors to differences in composition; conversely, calculation of the hygroscopic growth factor from composition will result in its overestimation for small drops by an

amount that is inversely proportional to  $r_{\text{dry}}$ . For drops with  $r_{\text{dry}} = (10, 15, 25)$  nm, comparable in size to the smallest values of the radius for which growth factors have been measured, the decrease due to the Kelvin effect in the hygroscopic growth factor from a low value of relative humidity to  $h = 0.9$  given by Eq. 22 is  $\sim(0.3, 0.2, 0.1)$ , an appreciable fraction of the growth factor itself. Hence for drops of these sizes it is important to take into account the Kelvin effect on the growth factor.

## 2.5 Comparison with Measurements of Ammonium Sulfate Solution Drops

The Kelvin effect on the equilibrium radius of an aqueous solution drop can be investigated through measurements of radii of very small drops. Such data have been reported as growth factors  $g(0, h)$  for ammonium sulfate solution for various values of fractional relative humidity  $h$ , measured using a differential mobility analyzer (DMA) by Hämeri *et al.* (2000) for dry radii of 4, 5, 7.5, 15, and 25 nm, and by T. Onasch (unpublished data) for dry radii of 2.4, 4.45, 10.0, 10.8, 25.15, and 27.3 nm. Some of these data are shown in Fig. 5. As the reported growth factors  $g(0, h)$  are ratios of the radius measured at  $h$  to the dry radius measured by a DMA, they refer to mobility radii and thus for nonspherical drops contain a shape factor. For this reason and for reasons discussed in the introduction, the measured dry radii of such drops are not necessarily equal to the values of  $r_{\text{dry}}$  as defined here, and thus these growth factors are not necessarily equal to radius ratios  $\xi(h)$ . However, for comparison purposes the measured dry radii are assumed equal to  $r_{\text{dry}}$  values, and the growth factors are thus assumed to be equal to, and compared with, radius ratios. It should also be noted that such a comparison is limited, as hygroscopic growth and density data are available for ammonium sulfate solution drops only down to values of water activity near 0.37, which for drops with  $r_{\text{dry}} = (5, 10, 25)$  nm correspond to values of  $h$  of approximately (0.48, 0.43, 0.39).

As expected, the growth factors of small drops are less than the growth factor of the bulk solution by an amount that increases with decreasing  $r_{\text{dry}}$  at a given  $h$ , and by an amount that increases with increasing  $h$  for a given  $r_{\text{dry}}$ . The decrease in the efflorescence relative humidity from the bulk value of  $\sim 0.37$  to near  $\sim 0.30$  is evident for drops with  $r_{\text{dry}} = 10$  and 25 nm, and no efflorescence is apparent for drops with  $r_{\text{dry}} = 5$  nm. The scatter within each size range of dry radius is a few percent, and for the most part the two data sets are consistent with each other, although for relative humidities less than  $\sim 0.6$  the growth factors of Onasch for dry radii 4.5 nm are a few ( $\sim 4$ -5) percent lower than those of Hämeri *et al.* for dry radii 4 nm and 5 nm. For drops with  $r_{\text{dry}} = 10$  nm and 25 nm the agreement between the theoretical prediction and the measurements is quite good above  $h \approx 0.6$ , and within  $\sim 2\%$  at lower  $h$ . For drops with  $r_{\text{dry}} = 5$  nm the theoretical prediction yields values of the radius ratio for  $h < 0.6$  that are greater than the measurements of Hämeri *et al.* by  $\sim 2\%$  and those of Onasch by  $\sim 5\%$ , although at higher values of  $h$  the agreement is better.

There are several possible reasons for the small differences between theory and measurement. Some of the differences might be attributed to the measurements themselves; Hämeri *et al.* noted that their measured values differed somewhat from those determined from electrodynamic balance measurements (from which the vast majority of hygroscopic data in the supersaturated regime have been determined). Uncertainties in measured radii were stated by Onasch to be 1-2%, and those of Hämeri *et al.* were

probably similar. Another factor that might contribute to the differences between the measurements and theory is the large extrapolation required for the surface tension. As the Kelvin effect increases the value of  $h$  for which saturation with respect to the solute occurs from 0.80 for bulk ammonium sulfate solutions (for which  $\xi = 1.49$ ) to  $h = (1.03, 0.91, 0.84)$  for drops with  $r_{\text{dry}} = (5, 10, 25)$  nm, most of the measurements were of drops that were supersaturated, and thus required extrapolations of the surface tension for comparisons. The surface tension of the ammonium sulfate solution-air interface at saturation ( $a_w=0.80$ ) is  $\sim 20\%$  greater than that of pure water, and the extrapolation used (Appendix 1) yields an increase of nearly 60% over that of pure water at  $a_w = 0.4$ . This is a rather large extrapolation, although to account for the difference between the trend of the data and theory for values of  $h$  in the range 0.4-0.6 would require that the dependence of surface tension on concentration be even greater, by more than a factor of two. Contributions to the differences between measurement and theory may also arise from the assumption that the measured dry radii, which are mobility radii measured by DMAs, are equal to values of  $r_{\text{dry}}$  as defined here. Overestimation of measured dry radii, such as could occur if the dried particles were not spherical or if they contained inclusions or any surface water, would result in underestimation of the radius ratios. Investigators have noted that small particles may contain some water, either as inclusions or on the surface, even when at relative humidities at which they are expected to be dry (Cziczo *et al.*, 1997; Weis and Ewing, 1999; Cziczo and Abbatt, 2000). With regard to surface water uptake, the consequences will be greater for smaller particles, and only a small amount of uptake would be required to account for the differences between measurements and theory. For example, a surface monolayer of water (of depth  $\sim 0.2$  nm) on a dry particle with radius 5 nm results in a 4% increase in the radius—enough to account for the difference for 5 nm drops.

In conclusion, the agreement between theory and experiment for small drops of ammonium sulfate is quite good—especially in view of possible measurement uncertainties, the extrapolations required, and the assumptions that the dried particles were spherical and that their radii were equal to the stated  $r_{\text{dry}}$  values—and the expected behavior with regard to Kelvin (surface tension) effects on equilibrium radius is seen to occur.

### 3. Previous Parameterizations of the Kelvin Effect

As noted above, any expression that gives the radius ratio  $\xi \equiv r/r_{\text{dry}}$  of an aqueous solution drop in terms of only the fractional relative humidity  $h$  cannot include the effect of surface tension, and hence must apply only to the bulk solution, as the only dimensionless parameters that occur in the relation are  $\xi$  and  $h$ . Conversely, any expression for the radius ratio that depends on  $r_{\text{dry}}$  necessarily implies that this dependency describes the effect of surface tension, and an additional quantity of dimension length (such as  $r_\sigma$ ) is required to express the relation in dimensionless form. By expressing the relationship between  $\xi$  and  $h$  in terms of the ratio  $\xi_\sigma \equiv r_\sigma/r_{\text{dry}}$  this dependency can be explicitly determined. Several empirical expressions for the radius ratio as a function of relative humidity that include a dependency on  $r_{\text{dry}}$  (and thus implicitly include the Kelvin effect) have previously been presented, although none of

these expression has a physical basis and none contains an explicit dependence on surface tension.

An expression for the radius ratio for a number of different inorganic solutes presented by Fitzgerald (1975) can be written in the form  $\xi = \alpha r_{\text{dry}}^{\beta-1}$ , where  $\alpha = C \exp[0.066h/(\Phi-h)]$ ,  $C$  is a constant that depends only on the solute,  $\Phi$  is a function of  $h$ , and  $\beta = \exp[0.00077h/(1.009-h)]$  for all substances considered. The value of  $\alpha$  and therefore that of  $C$  depend on the dimensions of  $r_{\text{dry}}$ , which must be expressed in units of micrometers for the constants presented by Fitzgerald. The limits of validity of this formulation were stated as  $h = 0.81-0.995$  and  $r_{\text{dry}} = 0.05-3 \mu\text{m}$ , and it was further stated that the accuracy of this approximation decreases rapidly outside the limits. According to this formulation the ratio of the radii at two values of  $h$  (*i.e.*, the growth factor) depends only on  $r_{\text{dry}}$  and is independent of the solute, in contrast to the known behavior of solutions of these solutes. The effect of surface tension is contained in the factor  $r_{\text{dry}}^{\beta-1}$ , but as there is no characteristic length scale in this formulation, it is not possible to write this factor in dimensionless form, which would explicitly indicate the dependence on radius of surface tension and other pertinent quantities. As  $\beta-1$  takes its maximum value of 0.056 at  $h = 0.995$  (for  $r_{\text{dry}}$  in micrometers), the factor containing the effect of surface tension on the radius ratio, which can be written as  $\exp[(\beta-1)\ln r_{\text{dry}}]$ , can be accurately approximated over the stated range of validity as  $1+(\beta-1)\ln(r_{\text{dry}}/\mu\text{m})$ . Thus according to this formulation the lowest-order correction to the radius due to surface tension is directly proportional to  $(r_{\text{dry}})(\ln r_{\text{dry}})$ , implying that for sufficiently large drops at a given  $h$  this lowest-order correction increases with increasing  $r_{\text{dry}}$  instead of being independent of  $r_{\text{dry}}$  as determined above.

The results of Fitzgerald for sea salt aerosol particles for  $r_{\text{dry}}$  from 0.1  $\mu\text{m}$  to over 100  $\mu\text{m}$  were fitted by Andreas (1989, 1990) under the assumption that they behaved similarly to sodium chloride solution drops, yielding two expressions (depending on how Fitzgerald's results were fitted) for the ratio of the radius of a drop at  $h = 0.80$  to that at  $h = 0.98$ ,

$$\frac{r(0.80)}{r(0.98)} = 0.5175[r(0.98)]^{-0.0244}$$

and

$$\frac{r(0.80)}{r(0.98)} = 0.4954[r(0.98)]^{0.0029},$$

where  $r(0.98)$  is in micrometers. As no characteristic length scale is contained in these expressions it is not possible to present them in dimensionless form to explicitly indicate the dependence on surface tension. Under the assumption that sea salt aerosol particles have similar hygroscopic growth behavior to drops of sodium chloride, for which  $\xi(0.98) = 4.0$  and  $\xi(0.80) = 2.0$  for bulk solutions, the ratio  $r(0.80)/r(0.98)$  is approximately  $0.50-(0.002 \mu\text{m})/r_{\text{dry}}$ , whereas the expressions presented by Andreas can be transformed to yield  $0.50-0.012[\ln(r_{\text{dry}}/\mu\text{m})]$  and  $0.50+0.0014[\ln(r_{\text{dry}}/\mu\text{m})]$  for this ratio (to lowest order). Thus according to these expressions the lowest-order correction to the radius due to surface tension does not approach zero with increasing  $r_{\text{dry}}$ , as determined above.

Another expression for the drop radius as a function of fractional relative humidity  $h$  up to and including values of  $h$  equal to unity, and thus implicitly including

the Kelvin effect, was proposed by Gerber (1985). Although this expression provides rather accurate values for the radius ratio as  $h$  approaches unity, it was not presented in dimensionless form which would allow the dependence on surface tension to be explicitly determined, and it does not provide the correct lowest-order correction to the radius ratio at values of  $h$  far from unity. This expression is discussed further in Lewis (2006).

#### 4. Summary

Although the effect of surface tension on the equilibrium vapor pressure above an aqueous solution drop (Kelvin effect) is easily quantified and has long been known, no formula for the decrease in the equilibrium radius of a drop due to the Kelvin effect has previously been reported, and the previous expressions parameterizing the Kelvin effect on radius do not yield the correct functional dependence of radius ratio on  $r_{\text{dry}}$ . As this equilibrium radius is a key property of atmospheric aerosol particles, and as measurements of smaller particles become more common, the Kelvin effect on the equilibrium radius, and accurate estimates quantifying this effect, become increasingly important. Broadly applicable expressions for the change in this equilibrium radius have been presented as a function of relative humidity (RH), together with an approximation that is accurate over a wide range of relative humidities and drop sizes. The novel result was obtained that at a given RH the lowest-order change in the equilibrium radius resulting from the Kelvin effect is independent of the mass of solute in the drop and depends only weakly on the composition of the solute. This decrease in radius ranges from ~0.35 nm at 50% RH to ~3 nm at 90% RH and ~35 nm at 99% RH. Formulae are also presented for the range of dry radii for which the Kelvin effect results in more than a given fractional increase at a given RH, and for the decrease in the hygroscopic growth factor as a function of dry radius resulting from the Kelvin effect. These results readily allow determination of the range of relative humidities and particle sizes for which the Kelvin effect is important and of the magnitude of this effect on the equilibrium dry radius and on the hygroscopic growth factor.

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## References

- Andreas, E. L. (1989). Thermal and size evolution of sea spray drops, pp. 37, U. S. Army Cold Regions Research and Engineering Laboratory Report.
- Andreas, E. L. (1990). Time constants for the evolution of sea spray droplets, *Tellus*, 42B, 481-497.
- Berg, O. H., Swietlicki, E., & Krejci, R. (1998). Hygroscopic growth of aerosol particles in the marine boundary layer over the Pacific and Southern Oceans during the First Aerosol Characterization Experiment (ACE 1). *Journal of Geophysical Research*, 103(D13), 16535-16545.
- Clegg, S. L., Ho, S. S., Chan, C. K., & Brimblecombe, P. (1995). Thermodynamic properties of aqueous  $(\text{NH}_4)_2\text{SO}_4$  to high supersaturation as a function of temperature. *Journal of Chemical and Engineering Data*, 40, 1079-1090.
- Clegg, S. L., Brimblecombe, P., Liang, Z., & Chan, C. K. (1997). Thermodynamic properties of aqueous aerosols to high supersaturation: II—A model of the system  $\text{Na}^+ \text{Cl}^- \text{NO}_3^- \text{SO}_4^{2-} \text{H}_2\text{O}$  at 298.15K. *Aerosol Science and Technology*, 27, 345-366.
- Covert, D., & Heintzenberg, J. (1993). Size distributions and chemical properties of aerosol at Ny Ålesund, Svalbard. *Atmospheric Environment*, 27A(17/18), 2989-2997.
- Cziczo, D. J., Nowak, J. B., Hu, J. H., & Abbatt, J. P. D. (1997). Infrared spectroscopy of model tropospheric aerosols as a function of relative humidity: Observation of deliquescence and crystallization. *Journal of Geophysical Research*, 102(D15), 18843-18850.
- Cziczo, D. J., & Abbatt, J. P. D. (1999). Infrared observation of the response of NaCl,  $\text{MgCl}_2$ ,  $\text{NH}_4\text{HSO}_4$ , and  $\text{NH}_4\text{NO}_3$  aerosols to changes in relative humidity from 298 to 238 K. *Journal of Physical Chemistry*, A104, 2038-2047.
- Fitzgerald, J. W. (1975). Approximation formulas for the equilibrium size of an aerosol particle as a function of its dry size and composition and the ambient relative humidity. *Journal of Applied Meteorology*, 14, 1044-1049.
- Gasparini, R., Li, R., & Collins, D. R. (2004). Integration of size distributions and size-resolved hygroscopicity measured during the Houston Supersite for compositional categorization of the aerosol. *Atmospheric Environment*, 38, 3285-3303.
- Hämeri, K., Väkevä, M., Hansson, H.-C., & Laaksonen, A. (2000). Hygroscopic growth of ultrafine ammonium sulfate aerosol measured using an ultrafine tandem differential mobility analyzer. *Journal of Geophysical Research*, 105(D17), 22231-22242.

- Kasten, F. (1969). Visibility forecast in the phase of precondensation. *Tellus*, 21, 631-635.
- Keith, C. H., & Arons, A. B. (1954). The growth of sea salt particles by condensation of atmospheric water vapor. *Journal of Meteorology*, 11, 173-184.
- Köhler, H. (1936). The nucleus in and the growth of hygroscopic droplets. *Transactions of the Faraday Society*, 32, 1152-1161.
- Korhonen, P., Laaksonen, A., Batris, E., & Viisanen, Y. (1998). Thermodynamics for highly concentrated water-ammonium sulfate solutions. *Journal of Aerosol Science*, 29(Suppl. 1), S379-380.
- Lamb, H. (1932). *Hydrodynamics*. Sixth Edition. Cambridge University Press. 738 p.
- Lewis, E. R. (2006). Parameterizations for the equilibrium radius of a hygroscopic aerosol particle as a function of relative humidity up to relative humidity 100% including the effect of surface tension (Kelvin effect). *Journal of Aerosol Science (to be submitted)*.
- Lewis, G. N., & Randall, M. (1961). *Thermodynamics*. Second Edition (revised by K. S. Pitzer and L. Brewer). McGraw-Hill Book Company. New York. 713 p.
- McMurry, P. H., & Stolzenburg, M. R. (1989). On the sensitivity of particle size to relative humidity for Los Angeles aerosols. *Atmospheric Environment*, 23(2), 497-507.
- Rayleigh, Lord (1879). On the equilibrium of liquid conducting masses charged with electricity. *Philosophical Magazine*, 14, 184-186.
- Svenningsson, B., Hansson, H.-C., Martinsson, B., Wiedensohler, A., Swietlicki, E., Cederfelt, S.-I., Wendisch, M., Bower, K. N., Choularton, T. W., & Colville, R. N. (1997). Cloud droplet nucleation scavenging in relation to the size and hygroscopic behaviour of aerosol particles. *Atmospheric Environment*, 31(16), 2463-2475.
- Swietlicki, E., Zhou, J., Covert, D. S., Hämeri, K., Busch, B., Väkeva, Dusek, U., Berk, O. H., Wiedensohler, A., Aalto, P., Mäkelä, J., Martinsson, B. G., Papaspiropoulos, G., Mentes, B., Frank, B., & Stratmann, F. (2000). Hygroscopic properties of aerosol particles in the north-eastern Atlantic during ACE-2. *Tellus*, 52B, 201-227.
- Tang, I. N. (1976). Phase transformation and growth of aerosol particles composed of mixed salts. *Journal of Aerosol Science*, 7, 361-371.
- Tang, I. N. (1996). Chemical and size effects of hygroscopic aerosols on light scattering coefficients. *Journal of Geophysical Research*, 101(D14), 19245-19250.

- Tang, I. N., & Munkelwitz, H. R. (1994). Water activities, densities, and refractive indices of aqueous sulfates and sodium nitrate droplets of atmospheric importance. *Journal of Geophysical Research*, 99(D9), 18801-18808.
- Thomson, S. W. (1871). On the equilibrium of vapour at a curved surface of liquid. *Philosophical Magazine*, 4, 448-452.
- Weis, D. D., & Ewing, G. E. (1999). Water content and morphology of sodium chloride aerosol particles. *Journal of Geophysical Research*, 104(D17), 21275-21285.
- Wright, H. L. (1936). The size of atmospheric nuclei: some deductions from measurements of the number of charged and uncharged nuclei at Kew Observatory. *Proceedings of the Physical Society*, 48(5), 675-688.
- Young, T. F., & Harkins, W. D. (1928), in International Critical Tables, Vol. 4 (Edited by Washburn, E. W.), National Research Council.
- Zhang, X. Q., McMurry, P. H., Hering, S. V., & Casuccio, G. S. (1993). Mixing characteristics and water content of submicron aerosols measured in Los Angeles and at the Grand Canyon. *Atmospheric Environment*, 27A(10), 1593-1607.

## Appendix 1. Surface tension of supersaturated solutions.

The dependencies on solute concentration of the partial molal volume of water in solution  $\bar{v}_w$  and of the surface tension of the solution-air interface  $\sigma$ , and hence of  $r_\sigma$ , are required for evaluation of various expressions and quantities plotted in this paper. These dependencies are accurately known for bulk solutions that are subsaturated with respect to the solute (i.e., water activities greater than 0.80 for ammonium sulfate and 0.75 for sodium chloride), and accurate measurements have been reported for densities (from which the partial molal volumes of water can be calculated) of supersaturated solutions of ammonium sulfate (Tang and Munkelwitz, 1994b) and sodium chloride (Tang, 1996), but no measurements have been reported for the surface tension in the supersaturated regime. Hence values that are used for surface tension for solutions that are supersaturated with respect to the solute are necessarily extrapolations.

One expression for the surface tension for supersaturated ammonium sulfate solutions is that proposed by Korhonen *et al.* (1998), a seventh-order polynomial in solute mass fraction based primarily on six values of  $\Delta\sigma (\equiv \sigma - \sigma_w)$  for subsaturated ammonium sulfate solutions from Vol. 4 of International Critical Tables (Young and Harkins, 1928, p. 464). However, as these data could be fitted to a single-parameter expression (in molality) to within stated uncertainties (3-9%), it would appear that little justification can be made for this mode of extrapolation. The alternative approach taken here for evaluation of the dependence on solute concentration of the surface tension of supersaturated solutions of both ammonium sulfate and sodium chloride for use in Figs. 2 and 3 was to linearly extrapolate the relative humidity dependence of the surface tension of subsaturated solutions to relative humidities below the bulk deliquescence values. This approach was taken based on the observation that these linear relations provide good fits in the subsaturated regimes.

Values of surface tension and partial molal volume of water and of  $r_\sigma$  relative to those for pure water are shown in Table A1 for solutions of ammonium sulfate and sodium chloride at water activity  $a_w$  corresponding to saturation (i.e., bulk deliquescence) and to efflorescence (these are extrapolated values), from which it can be seen that the dependence of  $r_\sigma$  on concentration is determined primarily by that of surface tension and to a much lesser extent by that of the partial molal volume of water. The values of the surface tension, and thus of  $r_\sigma$ , require large extrapolations for relative humidities below 0.80 (ammonium sulfate) or 0.75 (sodium chloride), but as the decrease in radius due to the Kelvin effect at these relative humidities is  $\sim 1$  nm or less, for a wide range of drop sizes the consequences of uncertainty in the extrapolations are not important.

A possible approach that could be used to determine the surface tension of supersaturated solutions and its dependence on concentration is to measure the resonant frequencies of shape oscillations of a supersaturated solution drop suspended in an electrodynamic balance. The resonant frequency of the  $j^{\text{th}}$  mode of such an oscillation for an isolated drop of radius  $r$ , density  $\rho$ , and surface tension  $\sigma$ , and containing charge  $q$ , is given by

$$\frac{f_j}{\text{Hz}} = \frac{1}{2\pi} \left[ \frac{j(j-1)(j+2)}{\rho r^3} \right]^{1/2} \left[ \sigma - \frac{q^2 \left( 1 - \frac{1}{\varepsilon} \right)}{16\pi\varepsilon_0 r^3 (j+2)} \right]^{1/2} \quad (\text{A1})$$

(Rayleigh, 1882), where  $\varepsilon$  is the dielectric constant of the solution and  $\varepsilon_0$  is the electric constant, also known as the permittivity of free space. For a stable drop the term containing the charge on the drop in Eq. A2 must be less than the surface tension (although the effect of charge typically has negligible effect on the equilibrium vapor pressure of a drop in an electrodynamic balance, its effect on the resonant frequency of oscillation might not be negligible). The charge can be obtained for a given situation from characteristics of the electrodynamic balance. The lowest nonzero frequency, which occurs for the mode with  $j = 2$ , is given by

$$\frac{f_2}{\text{Hz}} = \left( \frac{2}{\pi^2 \rho r^3} \right)^{1/2} \left[ \sigma - \frac{q^2 \left( 1 - \frac{1}{\varepsilon} \right)}{64\pi\varepsilon_0 r^3} \right]^{1/2}; \quad (\text{A2})$$

for a typical values for density  $1.5 \text{ g cm}^{-3}$  and surface tension  $100 \text{ g s}^{-2}$ , Eq. A2 yields  $\sim 10^5 \text{ Hz}$  for the lowest nonzero resonant frequency for a drop with  $r = 10 \text{ }\mu\text{m}$  and  $\sim 3 \cdot 10^5 \text{ Hz}$  for a drop with  $r = 5 \text{ }\mu\text{m}$ , if the term containing the charge can be neglected. Eq. A2 can be inverted to yield an expression for the surface tension

$$\sigma = \frac{\pi^2 \rho r^3 f_2^2}{2} + \frac{q^2 \left( 1 - \frac{1}{\varepsilon} \right)}{64\pi\varepsilon_0 r^3}, \quad (\text{A3})$$

which allows determination of surface tension from measurement of the resonant frequency together with knowledge of the radius, density, and charge (results are insensitive to the value of  $\varepsilon$  as it is typically much greater than unity). This method might also be employed to determine the kinematic viscosity of the solution  $\nu$ , as an unforced shape oscillation of mode  $j$  of a drop decays exponentially with characteristic time  $\tau_j$  given by

$$\tau_j = \frac{r^2}{(j-1)(2j+1)\nu} \quad (\text{A4})$$

(Lamb, 1932, §355).

Table 1

Solute	$h$ range	$n$	$c$	Accuracy
$(\text{NH}_4)_2\text{SO}_4$	0.40-0.90	0.22	1.05	1%
	0.90-0.995	1/3	0.81	3%
NaCl	0.45-0.90	0.265	1.31	1%
	0.90-0.995	1/3	1.09	3%

Table 1. Parameters for the power law relationship between radius ratio and  $1-h$  given by Eq. 9 and approximate accuracy in different ranges of fractional relative humidity  $h$  for aqueous solutions of ammonium sulfate,  $(\text{NH}_4)_2\text{SO}_4$ , and sodium chloride, NaCl.

Table A1

Solute	$a_w$	$\frac{\sigma}{\sigma_w}$	$\frac{\bar{v}_w}{\bar{v}_{w,0}}$	$\frac{r_\sigma}{r_{\sigma,0}}$
pure water	1	1	1	1
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	0.80	1.20	0.96	1.15
	0.40	1.55*	0.90	1.40*
NaCl	0.75	1.15	0.99	1.15
	0.45	1.30*	0.97	1.25*

Table A1. Values of the surface tension  $\sigma$ , partial molal volume of water  $\bar{v}_w$ , and  $r_\sigma$  relative to those of pure water ( $\sigma_w$ ,  $\bar{v}_{w,0}$ , and  $r_{\sigma,0}$ , respectively) for aqueous solutions of ammonium sulfate, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, and sodium chloride, NaCl, at water activities  $a_w$  corresponding to saturation and to efflorescence (crystallization). Values of the surface tension and hence  $r_\sigma$  for supersaturated solutions (denoted by asterisks) are extrapolations based on linear relations for subsaturated solutions.

Fig. 1.

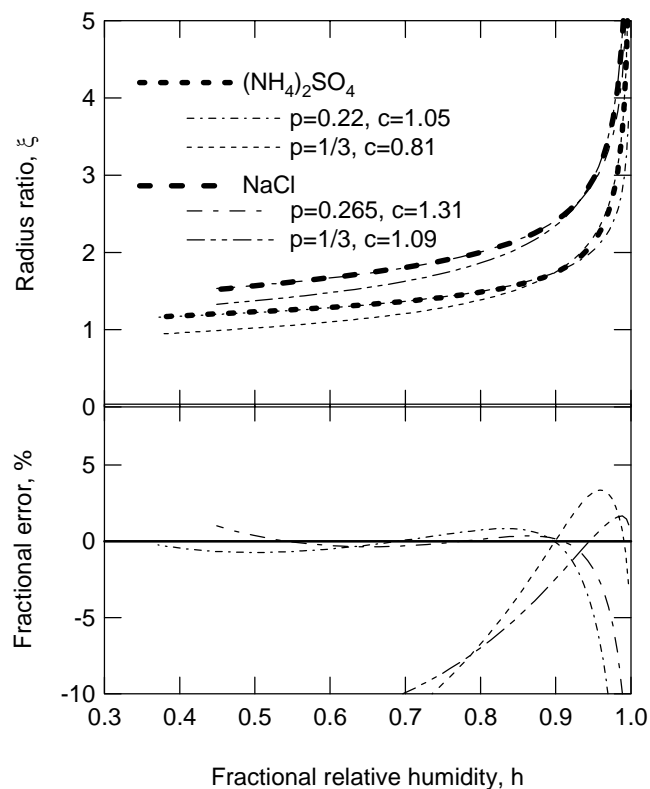


Fig. 1. Radius ratio (relative to volume-equivalent dry radius),  $\xi \equiv r/r_{\text{dry}}$ , of solution drops of ammonium sulfate,  $(\text{NH}_4)_2\text{SO}_4$  (based on water activities reported by Clegg *et al.*, 1995, and densities reported by Tang and Munkelwitz, 1994) and sodium chloride,  $\text{NaCl}$  (based on water activities reported by Clegg *et al.*, 1997, and densities reported by Tang, 1996), at 25°C. Also shown are power law approximations (Eq. 12) with coefficients chosen to provide good fits in two ranges of fractional relative humidity  $h$ :  $h_e < h < 0.90$  (where  $h_e$  is the efflorescence, or crystallization, relative humidity;  $\sim 0.4$  for ammonium sulfate solutions and  $\sim 0.45$  for sodium chloride solutions), and  $0.90 < h < 0.995$  (the upper limit of measurements), as a function of fractional relative humidity (upper panel). Lower panel shows fractional error in the fits.



Fig. 2.

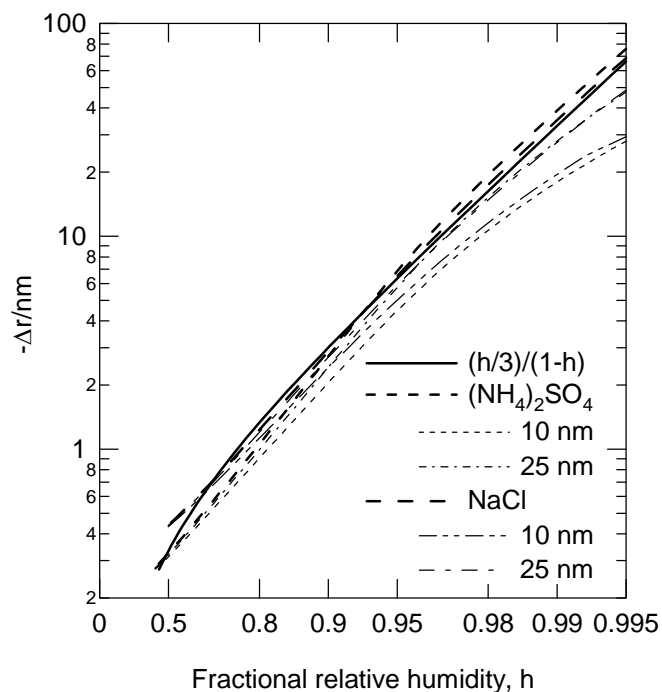


Fig. 2. Lowest-order decrease in radius due to Kelvin effect  $-\Delta r$  as a function of fractional relative humidity  $h$  (plotted as the logarithm of  $1-h$ ) for approximation given by Eq. 15 and for aqueous solutions of ammonium sulfate,  $(\text{NH}_4)_2\text{SO}_4$ , and sodium chloride,  $\text{NaCl}$ . Also shown are decreases in the radius due to the Kelvin effect for ammonium sulfate and sodium chloride solution drops with  $r_{\text{dry}} = 10 \text{ nm}$  and  $25 \text{ nm}$  calculated from Eq. 1, with the dependencies of the partial molal volume of water in solution and the surface tension of the solution-air interface on concentration are taken into account as discussed in the text; values of the surface tension  $\sigma$  for solutions that are supersaturated with respect to the solute (relative humidities below the bulk deliquescence values 0.80 for ammonium sulfate and 0.75 for sodium chloride) were extrapolated from fits to  $\sigma$  vs.  $h$  based on measurements on subsaturated solutions as discussed in Appendix 1.

Fig. 3.

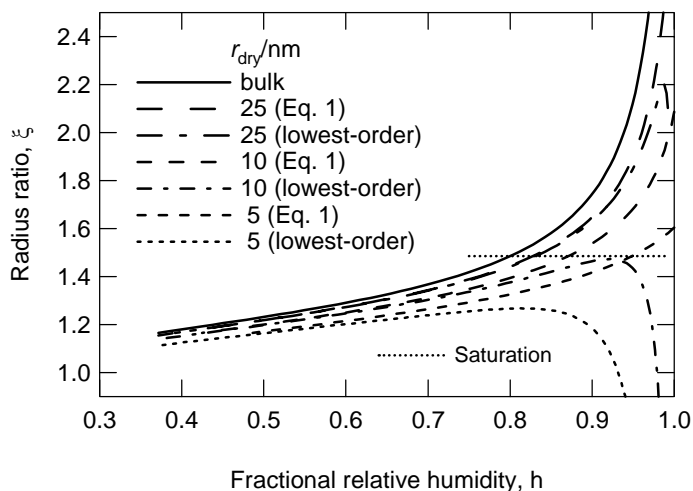


Fig. 3. Radius ratio  $\xi$  as a function of fractional relative humidity  $h$  for bulk solution of ammonium sulfate,  $(\text{NH}_4)_2\text{SO}_4$  (based on water activities reported by Clegg *et al.*, 1995, and densities reported by Tang and Munkelwitz, 1994), for ammonium sulfate solution drops with  $r_{\text{dry}}$  values of 5, 10, and 25 nm calculated from Eq. 1, and for ammonium sulfate solution drops of these sizes calculated using Eq. 8 as the lowest-order correction due to the Kelvin effect from the bulk solution. For the radius ratios of the solution drops the dependencies of the partial molal volume of water in solution and the surface tension of the solution-air interface on concentration are taken into account as discussed in the text; values of the surface tension  $\sigma$  for solutions that are supersaturated with respect to the solute (radius ratios below dotted line at  $\xi=1.49$ ) were extrapolated from fits to  $\sigma$  vs.  $h$  based on measurements on subsaturated solutions as discussed in Appendix 1.

Fig. 4

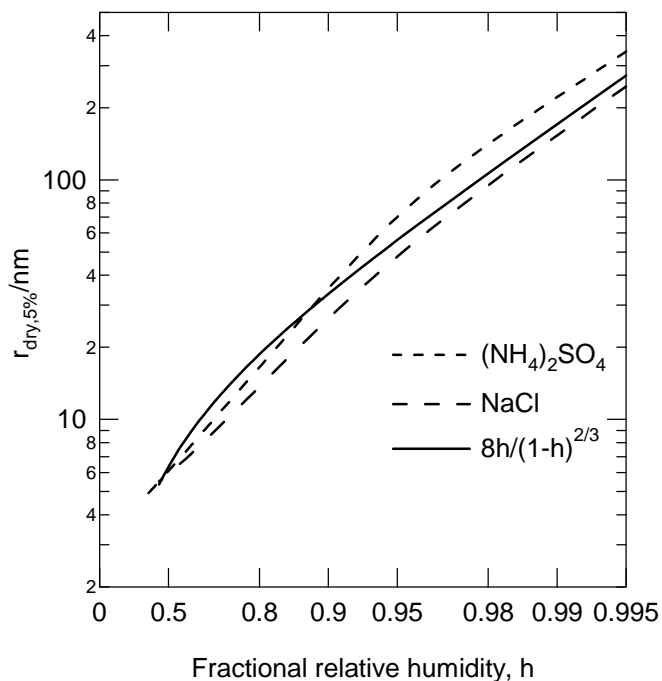


Fig. 4. Volume-equivalent dry radius  $r_{\text{dry},5\%}$  below which the Kelvin effect results in a decrease in the equilibrium radius greater than 5% for a given fractional relative humidity  $h$  (plotted as the logarithm of  $1-h$ ) for approximation given by Eq. 18 and for aqueous solutions of ammonium sulfate,  $(\text{NH}_4)_2\text{SO}_4$ , and sodium chloride,  $\text{NaCl}$ . For solutions of ammonium sulfate and sodium chloride the dependencies of the partial molal volume of water in solution and the surface tension of the solution-air interface on concentration are taken into account as discussed in the text; values of the surface tension  $\sigma$  for solutions that are supersaturated with respect to the solute (relative humidities below the bulk deliquescence values 0.80 for ammonium sulfate and 0.75 for sodium chloride) were extrapolated from fits to  $\sigma$  vs.  $h$  based on measurements on subsaturated solutions as discussed in Appendix 1.

Fig. 5

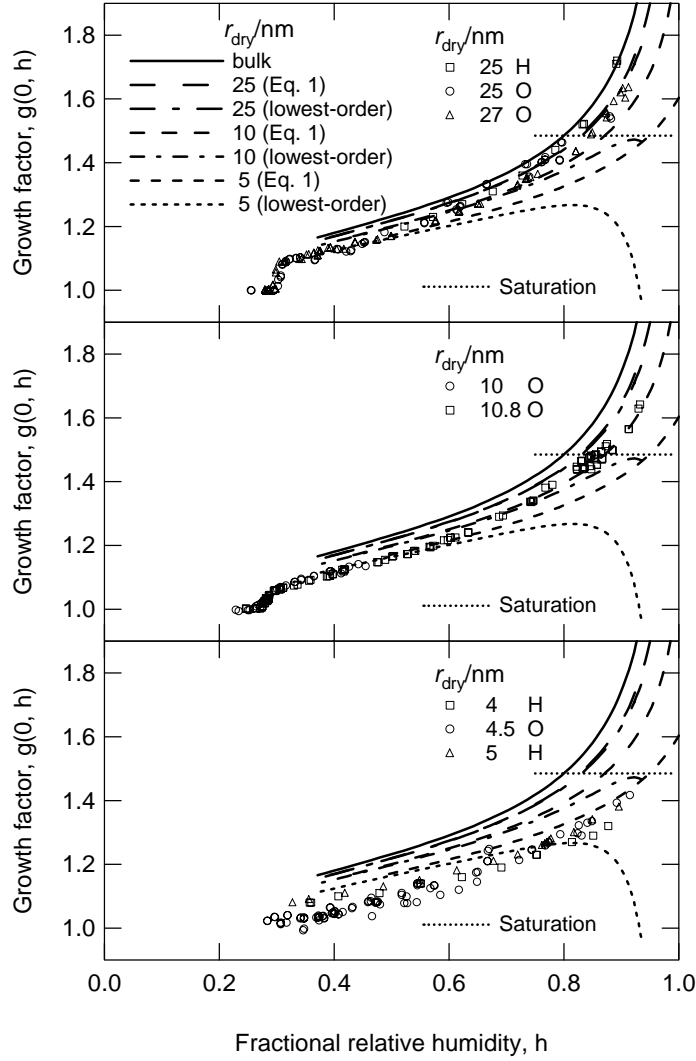


Fig. 5. Growth factors  $g(0, h)$  for ammonium sulfate solution drops at fractional relative humidity  $h$  relative to measured radii at  $h=0$  from Hämeri *et al.* (2000) for dry radii of 4, 5, and 25 nm (H) and from T. Onasch (unpublished data) for dry radii of 4.5, 10, 10.8, 25.15, and 27.3 nm (O). Curves for radius ratio  $\xi$  are as in Fig. 3. For comparison purposes it is assumed that the measured dry radius is equal to  $r_{\text{dry}}$ , although as discussed in the text the two quantities may not be identical.